FUNCTIONALIZED CARBON NANOTUBE SPONGE AS SULFUR RESERVOIR FOR LITHIUM SULFUR BATTERY

A Thesis

by

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ABSTRACT

Lithium sulfur batteries offer many advantages such as high specific capacity, environmental friendliness and low cost. However, several problems limit their commercialization, like low sulfur utilization because of the insulating nature of sulfur, and capacity degradation caused by dissolution of the intermediate product, polysulfide. Herein, we proposed that unzipping the carbon nanotube electrode to increase its surface area can enhance sulfur utilization due to the larger contact area. Furthermore, graphene oxide was chosen as a polysulfide immobilizer due to the electrostatic interaction between graphene oxide and polysulfide. Our results show much better battery cycle performance after the treatments just mentioned before, which are reliable supports for the hypothesis.

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NOMENCLATURE

CNT	Carbon Nanotube
Li-S	Lithium Sulfur
LIB	Lithium Ion Battery
GO	Graphene Oxide
3D	3-Dimensional
SCCM	Standard Cubic Centimeter per Minute
DOL	Dioxolane
DME	Dimethoxyethane
LiTFSI	Lithium Bis(trifluoromethane) Sulfonimide
EMIM BF4	1-ethyl-3-methyl Imidazolium Tetrafluoroborate
PVDF	Polyvinylidene Fluoride
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
BET	Brunauer–Emmett–Teller Analysis

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1. INTRODUCTION

1.1 Lithium Sulfur Battery

In modern society, one of the most important issues is to find a suitable energy storage device which can satisfy the gradually increasing demand from the devices such as portable electronic or electric vehicles.[1, 2] At the same time, the suitable device should be environmental friendly and low cost as well. Currently the most famous energy storage device for those application is lithium ion battery (LIB). The most reliable anode material of LIB is graphite due to its highly chemically stable nature and cost competitively, where lithium ion can diffuse into the interlayer and be encapsulated inside the graphite.[3] The anodic reaction can be represented as:

$$Li^+ + e^- + C_6 \rightleftharpoons LiC_6$$

In cathode, the most popular cathode materials of LIB is transitional metal oxides, such as $LiCoO_2$, $LiMn_2O$ and $LiFePO_4$. Taking $LiCoO_2$ as an example. The cathodic reaction of $LiCoO_2$ cathode is:

$$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^-$$

During the reaction, lithium ion can diffuse in and out from the interstitial sites in the crystal structure of transition metal oxide. The reaction is highly reversible, thus makes LIB rechargeable.[4]

However, those transitional metal oxides only possess specific capacity <200mAh/g because of the heavy transitional oxide matrix.[5] The low capacity gradually not able to fulfill the demand from the modern society. For example, the battery of iPad almost occupies half of its volume. It is urgent to find other candidates which possess much higher capacity than the current technology to meet the rapidly increasing requirement.

Lithium sulfur (Li-S) battery is a novel battery system which can provide much higher energy than LIB. It consists of lithium metal anode, sulfur cathode and organic electrolyte. Instead of the graphite anode in LIB, the lithium metal used in anode for Li-S battery, which has much higher specific capacity 3680mAh/g when comparing with the capacity of the most popular graphite anode (350mAh/g) of LIB. On the cathode side, sulfur possesses specific capacity as high as 1675mAh/g if fully discharged from S to Li_2S. It is much higher than the present cathode material of LIB we mentioned before since theoretically, one sulfur atom can incorporate two electrons, unlike most of the transitional metal oxide in LIB only can receive or release one electron.[6] The specific energy density of Li-S battery is about two times higher than the LIB, which is very competitive to those current battery technologies. It shows a great potential that it can provide enough energy for electric vehicles to travel more than 500km and meet the actual requirement. Besides, sulfur is abundant in the Earth's crust, which makes its price competitive than the transition metal oxide materials used in LIB. Furthermore, comparing with the transition metal oxide used in LIB, sulfur is much environmental friendly. Those factors make Li-S battery worth investigation. [7-9]

The following reaction is the overall reaction of Li-S battery:

$$2Li + S \rightleftharpoons Li_2S$$

When the battery is discharged, lithium ion will migrate from anode through electrolyte to cathode, at the same time electrons travel through the outside circuit to cathode, generates electricity. On cathode, sulfur is reduced by the electron and reacts with lithium ion, forms soluble lithium polysulfide (Li_2S_x, $3<x<8$) during discharge. The half reactions on the two electrodes are shown below:

Anodic reaction: $2Li \rightarrow 2Li^+ + 2e^-$

Cathodic reaction: $S + 2Li + 2e^- \rightarrow Li_2S$

The typical discharge process contains several different stages of reactions, which is shown as the two voltage plateau and one sloping region in the voltage profile. The intermediates form at the first plateau (voltage ~2.3V), slope region and second plateau are Li_2S_6, Li_2S_4 and Li_2S, respectively.[6, 10]

1.2 Challenges

Although sulfur has such many advantages, there are some important issues have to be solved in order to make the commercialization of Li-S battery possible. First, since sulfur is electrically insulating (conductivity ~10^{-30} S/cm), some conductive additives with high specific area have to be added into the electrode and mixed well with sulfur to transport electricity.[6] The most popular material serving as conductive matrix is carbon based material, such as active carbon, carbon black, carbon nanotube (CNT) and

graphene since carbon has the advantages such as chemically stability during the reaction, light weight and abundant.[11] Among these materials, CNT receives many attention because it has not only very high mechanical strength but also ultrahigh electrical conductivity.[5, 12-17] Besides, some binder have to be added into the material mixtures for binding the active materials together. During the cycle, the large volume change (~80%) of the active material will yield stress to the whole electrode, thus breaks the matrix apart.[6] So binder is necessary in most of the electrode designs to hold the other materials together and prevent failure. However, those binders such as polyvinylidene fluoride (PVDF) are general insulating.[14] Not only that, the chemically inert binder will serve as inactive material in the cathode, thus increases the electrode weight and reduces the specific energy density. It is necessary to develop a way to provide new matrix material which not only possess high specific surface area but also has binder-free structure.

Another issue has to be solved is the capacity fading due to the dissolution of reaction intermediate (lithium polysulfide Li_2S_x, $3<x<8$) into electrolyte, which is so called polysulfide shuttling.[2, 7, 16, 18-21] Those soluble intermediate products has high ionic mobility and can easily diffuse between the electrodes through electrolyte, reduces to insoluble forms such as Li_2S_2 and Li_2S at anode and deposits on the surface, causes capacity fading because of active material loss and insulating Li_2S_2 and Li_2S deposits on the electrode surface will block the lithium ions and electrons transportation, causes large impedance.[6, 21, 22] Furthermore, when the higher order lithium polysulfide can diffuse to the anode and react with lithium metal, and then reduces to lower order lithium

polysulfide and then diffuse back to cathode. The repeating mechanism will causes lower Coulombic efficiency because of the waste of electricity. Not only that, polysulfide shuttling will cause self discharge problem as well. Since during the resting, the dissolved polysulfide molecules will diffuse to anode and react with lithium, causes lower capacity and open circuit voltage.[6] Hence, it is necessary to find a suitable way to prevent polysulfide shuttling problem to make the Li-S battery system more promising.

Recent studies were focused on trapping sulfur in the carbonaceous nanostructures, such as mesoporous carbon, graphene, graphene oxide and CNT.[1, 5, 13-16, 20, 21, 23-25] It is well known that those small pores of the carbonaceous nanostructures can effectively limit the diffusion of polysulfide molecules, thus restrict them from diffuse out thus impede polysulfide shuttling. In this study, we choose CNT sponge made in our lab as the conductive matrix.[24, 26] It has several priorities when comparing with other carbon based material for Li-S battery cathode. First, it has the potential for bulk manufacturing. Different from other carbon nanomaterials such as graphene or single walled CNT, we can easily achieve gram of CNT sponge in just 1hr reaction time, and the cost is less than $1/gram.[27] Another advantage of CNT sponge is that unlike other carbon based materials need binder for binding the materials together, it possess 3-dimensional (3D) binder-free structure which can not only lower the cost of binder and decrease the unnecessary weight of binder but also enhance the electrical conductivity of cathode since most of the binders are insulating. Besides, its porous structure can confine the polysulfide molecules from escaping and then causes shuttle

effect.[15] Furthermore, its covalent bonded CNT structure can provide enough strength, thus it has the ability to endure the large volume change during the battery cycling and prevent the whole structure from breaking apart. [15, 26]

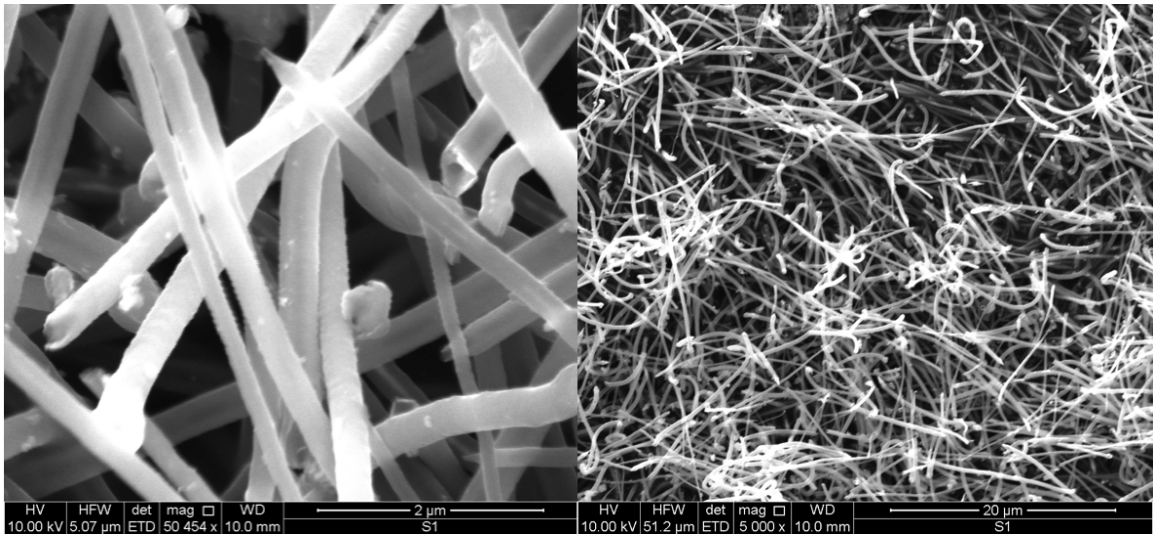

Fig. 1 SEM images of CNT sponge.

However, when comparing with other conductive matrix materials, the specific area of our CNT sponge is relatively lower to the others due to the large diameter of the CNT. Typically the range of the CNT diameter used as conductive matrix for Li-S battery in other literature is between 10~50nm, but ours is ~200nm, which is shown in Fig. 1. [13-15, 17, 25, 28] Since the rate of chemical reaction is proportional to the surface area, it is necessary to find a way to increase the specific surface area of the electrode, thus reaches the desired cell performance.[29] Vadahanambi et al. reported an ionic liquid assisted way to split CNT into graphene-like carbon nanosheet.[30] The reason why it is so called "ionic liquid" is because unlike other liquid in room temperature usually bonds by van der Waals forces, the bonding in ionic liquid is ionic bond.[31] They dispersed

CNT in a fluorine containing a kind of ionic liquid, 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIM BF4), and then did the microwave irradiation treatment in a conventional microwave oven at 700W for 240s. The high temperature created by the microwave irradiation will provide enough energy to activate the fluorine ion in the ionic liquid, thus attacks the defect sites, creates C-F bonding. After the bonding forms, it acts as nucleation sites for BF_4^- ions to attack, thus leads to the unzipping of CNT and forms graphene-like monolayer structure. Since the inner layer of CNT can be exposed after the unzipping, it should be a effective way to increase the specific surface area of CNTs, thus enhance the specific capacity of the Li-S battery. Not only that, it is reported the fluorine doping can increase the binding energy with lithium in Li_2S by the electrostatic force between the lithium and long pair electrons in fluorine.[32] The calculation result is shown below. Hence, the cycling performance can be further enhanced.

Polysulfide molecules not only can be trapped by porous carbon, there are many other different approaches for reducing polysulfide shuttling problems been reported. For example, Bauer et al.[33] developed a Nation coated separator to block polysulfide from transporting through the separator by reducing the pore size of the separator. Cheng et al. [11] adjusted the sulfur/electrolyte ratio to minimize the shuttling problem since the polysulfide solubility is related to the ratio. Tang et al.[13] reported a way about nitrogen-doped CNT as conductive matrix which can effectively reduce the sulfur loss from the cathode. The nitrogen-doped functional groups, such as pyridinic nitrogen and pyrrolic nitrogen, will have electrostatic interaction between the lone pair electrons on nitrogen and charged polysulfide molecule, thus catches the polysulfide from shuttling and reduces

the capacity fading. Wu et al.[34] used oxygen functionalized CNT as the matrix. The functional groups can effectively increase the bonding energy to the lithium sulfide. For example, the bonding energy they calculated between CNT and Li_2S is 0.00866 eV. On the other hand, the bonding energy between Li_2S and oxygen doped CNT is 0.39096 eV. And the bonding energy between CNT / S_4^{2-} and oxygen doped CNT / S_4^{2-} are 0.23160 eV and 0.51413 eV, respectively. The calculation is shown below. It is a strong evidence that the oxygen doping on CNT or graphene can effectively hinder the polysulfide shuttling problem.

Graphene oxide (GO), the oxidized product of graphene, is a two-dimensional monolayer carbon based material. The most common way to synthesize GO is so called Hummers' method, developed by William S. Hummers in 1958.[35] First, graphite and sodium nitrate are added into sulfuric acid in 66°C and then cooled to 0°C. Potassium permanganate is then added into it and then mixed well. Finally, water is added into the mixture. After cleaned the impurities, phosphorus pentoxide is added to get rid of the moisture.

Since it's the oxidized product of graphite, it has many oxygen containing functional groups, such as –OH, -COOH and -O-. As mentioned before, it is well known that these functional groups have the ability to adsorb lithium polysulfide, thus to prevent polysulfide shuttling issue.[16, 19, 20] Huang et al. developed a GO/CNT hybrid interlayer between the electrode and separator as polysulfide immobilizer and reached about 800mAh/g specific capacity after 100 cycles, where the one without GO/CNT hybrid interlayer sample only reached about 600mAh/g.[14] Zhang et al. developed a

GO/oxidized CNT coating on the separator to catch the polysulfide molecules, which shows significant capacity difference between the samples with and without GO / oxidized CNT coating. The one with GO/oxidized CNT coating possessed specific capacity about 800mAh/g whereas the other one only remained 300 mAh/g after 100 cycles.[36] Others also reached similar results that GO can effectively mitigate polysulfide shuttle problem.[23] It is because the lone pair electrons on the oxygen can have higher binding energy with lithium in Li_2S.[32]

Inspired by those references, we developed two different ways to enhance the cell performance. The first approach is to treat the CNT sponge with ionic liquid in high temperature for unzipping it, thus increases its surface area and reaches higher specific capacity. Due to it is hard to control the exact reaction condition such as temperature under microwave irradiation treatment, we choose using box furnace as the heating source instead of using microwave. Another approach is depositing a GO layer onto the electrode to adsorb the dissolved lithium polysulfide and then enhance the cell cyclability.

2. EXPERIMENTAL

2.1 CNT Sponge Synthesis

Ethylene gas (Airgas, 99.999%) and Ferrocene (Sigma Aldrich, 98%) were used as the carbon source and catalyst, respectively. CNT sponge was synthesized by a chemical vapor deposition (CVD) process inside a 1-inch diameter quartz tube, which was placed inside a 3-zone furnace (Lindberg/Blue M STF55346C). Ferrocene powder was inserted into the middle of zone 1. At the beginning, Ar (Airgas, 99.999%) was passed through the tube with 200 SCCM flow rate for 10 minutes to ensure no air was left inside the quartz tube. After that, the Ar flow was switched to H_2 flow with 260 SCCM flow rate. At the same time, the temperatures of zone 1 and zone 3 were raised to 120°C within 20min and 650°C within 10min, respectively. After the temperature reached the desired value, Ar passing through a water bubbler and C_2H_4 were passed into the quartz tube, both in 80 SCCM flow rate. Inducing water into the growth process can increase the catalyst lifetime, thus enhance the CNT growth.[12, 14] After a 1hr growth process, the furnace was cooled down with 200 SCCM Ar gas flow. Finally, ~1g of CNT sponge was obtained at zone 3.

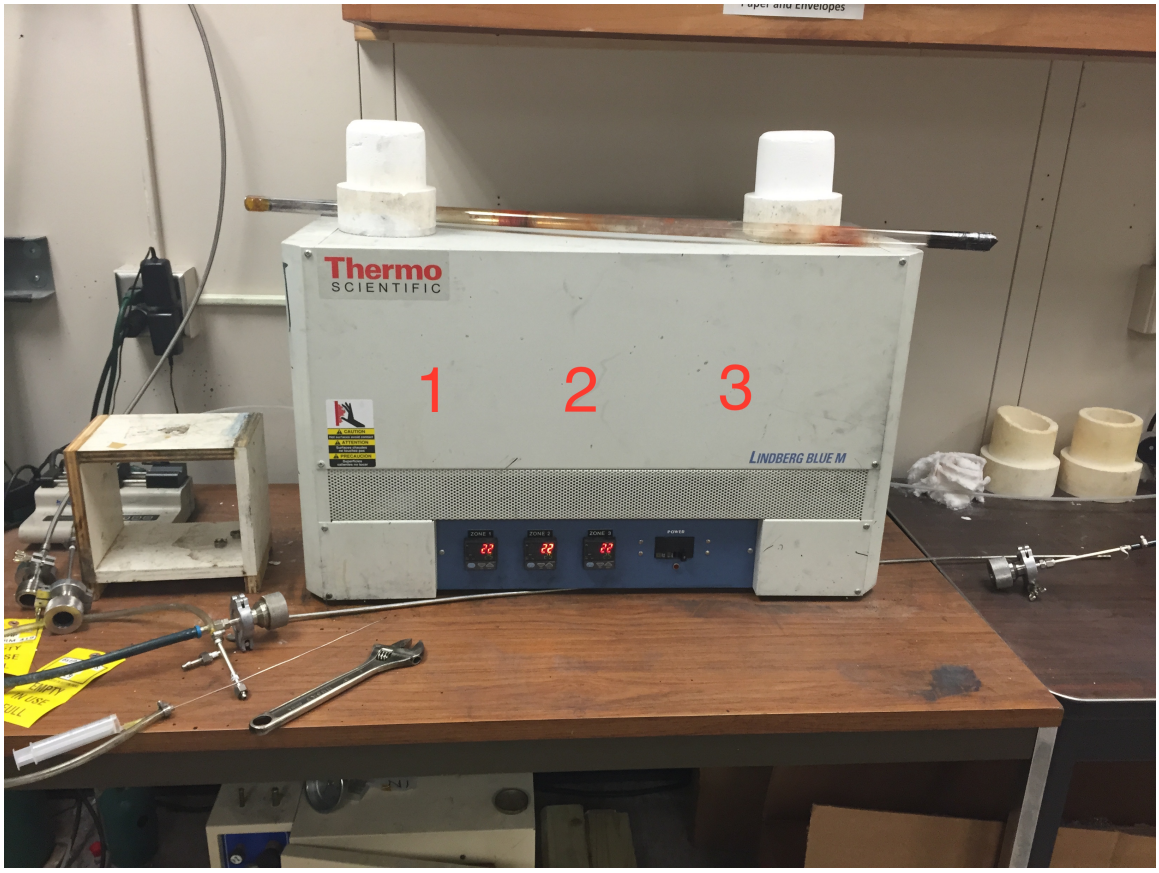

Fig. 2 The 3-zone furnace for CNT sponge synthesis.

2.2 Procedure of Unzipping CNT Sponge

CNT sponges were sliced into small circular pieces (9.5mm in diameter, 1mm in thickness) and immersed into EMIM BF4 (Sigma Aldrich, 99%) in a hydrothermal reactor, and then inserted into a box furnace (Lindberg/Blue M BF51894C-1) for heating. The temperature of the box furnace was raised from room temperature to 200°C within 20min, and then maintained at 200°C for desired time. The reason why we chose using box furnace instead of microwave as the heating source is because it is hard to precisely control the reaction conditions (such as temperature) when using microwave. Since the

power of the conventional microwave is too high for the tiny amount sample (<10mg), it only took several seconds for the ionic liquid to boil even when choosing the lowest power, thus makes reaction hard to control. Instead, the reactions done in box furnace showed much higher reproducibility. After the process was finished, the reactor was naturally cooled down to room temperature and then the unzipped CNT sponge was taken out and immersed into hot deionized water (~70°C) overnight several times to get rid of the EMIM BF4 residue. Finally, the CNT sponge was drying in a vacuum oven on ~60°C temperature overnight to ensure no water is left inside the sponge.

2.3 Sandwich Electrode Preparation

Sulfur powder (Alfa Aesar, 99.5%) was placed between two sliced circular CNT sponge (9.5mm in diameter, 1mm in thickness) with desired areal loading. The electrode was inserted between two flat stainless steel plates (15cm * 15cm) and pressurized for 10 min. The force was set to 4 tons. After the pressurizing, the sandwich electrode was reached and taken out. The sandwich structure can effectually prevent polysulfide shuttling problem by several mechanisms. Firstly, the two pieces of CNT sponges can act as current collector to provide good electrical conduction to sulfur. Besides, the porous structure of CNT sponge allows ions have enough path of diffusion to be effectively transported toward it. Not only that, the product during the cycling will be trapped inside the sandwich electrode.[37]

2.4 GO Layer Preparation

GO (Carbon Solutions, Inc.) was added into ethanol (EMD, 95%) and dispersed using the pen-type ultrasonic processor (Fisher Scientific Model 120) with 60W power for 30mins to reduce the self bundling of GO. The GO suspension was and then deposited onto the sandwich electrode by drop casting method. Sandwich electrode was placed onto hot plate, the temperature was set at 80°C to vaporize the excess ethanol inside the sponge. After reached the desired GO loading by repeating the previous procedures several times, the sandwich electrode was treated by a UV/ozone cleaner (Bioforce Nanosciences) for desired time to create defect sites on the GO layer, hence allows ions to transport through those defect sites instead of full block the paths.

2.5 Electrolyte Preparation

Dioxolane (DOL) (Alfa Aesar, 99%) and dimethoxyethane (DME) (Alfa Aesar, 99%) are mixed in 1:1 volume ratio as solvent for electrolyte. 1M lithium bis(trifluoromethane) sulfonimide (LiTFSI) (Sigma Aldrich, 99.995%) was added into the solvent as lithium salt for electrochemical reaction. It is the most popular electrolyte used in most of the Li-S battery related papers because its acceptable ion mobility and solvability of polysulfide. However, its Coulombic efficiency is usually less than 90%. [11] Hence, 0.5M $LiNO_3$ (Alfa Aesar, 99.999%) was added into the electrolyte to enhance the cycle life of the cell. It is well known that $LiNO_3$ can suppress the

polysulfide shuttle by forming a stable passivation layer on the lithium anode surface and enhance its Coulombic efficiency.[38, 39] All of the works were done in the argon filled glove box to prevent the influence of oxygen and moisture.

2.6 Synthesis of Electrolyte and Catholyte

The synthesis procedure of polysulfide catholyte (Li_2S_6) was described in our previous paper.[21] First, elemental sulfur and Li_2S (Sigma Aldrich, 99.98%) were mixed together with 5:1 molar ratio in the electrolyte. In order to fully dissolve Li_2S and sulfur, the mixture was heated by using sand bath to maintain the temperature at 90°C for 3 days under Ar atmosphere. Unlike the as-prepared mixture shows yellowish color, the color of fully dissolved catholyte turns to reddish.

2.7 Assembling and Testing of Cells

2032-type coin cell was used as the case for the battery testing. First, lithium metal foil was punched into circular shape with 1/2 inch diameter. And then a circular shape with 5/8 inch diameter Celgard 2400 separator was put on the top of lithium foil. The role of separator is to prevent anode and cathode form contacting with each other, thus causes short circuit. And then 60μL of electrolyte was added on top of the separator for wetting. After that, the CNT sponge cathode was stacked on top of the separator, followed by adding 40μL electrolyte to make sure all the two electrodes have enough

electrolyte. All of the assembling jobs were done in the glove box filled with argon due to the high reactivity between the lithium and oxygen. The testing was done by using Arbin BT2000 galvanostat. The cells were cycled at different rates (1C = 1600mA/g) with the cutoff voltage setting to 1.7V~3V during the cycling. Although for the entire reaction, the cutoff voltage can reach 1.5V when fully discharge, people usually increase cutoff voltage a little bit to prevent the fading of $LiNO_3$ additive.[6] The electrode morphology was inspected by scanning electron microscope (SEM) and transmission electron microscope (TEM) (JEOL 2010).

3. RESULTS AND DISCUSSION

3.1 Influence of Unzipping CNT

First, we would like to figure out the difference of our CNT sponge between before and after ionic liquid treatment. Fig. 3 shows the picture of CNT sponges before and after ionic liquid treatment, the reaction condition we chosen was 2hr treating time and 200°C treating temperature. The right one is before treatment, the left is after. After the ionic liquid treatment in the box furnace, the sponge still remained its original 3D structure instead of breaking into pieces (left), which indicates not all of the CNT in the CNT sponge is unzipped. In order to inspect the nanostructure difference, we took SEM and TEM to check it. Fig. 4 are the SEM and TEM images of CNT sponge after 2hr ionic liquid treatment. When comparing with the SEM image of pristine CNT sponge showed in Fig. 1, there were some part that the diameter of CNT was increased, which is indicated by the red arrow in Fig. 4. When we see the TEM image, it is obvious that the CNTs were fractured and formed nanosheets instead of tube-like structure after the treatment, which is the same as the previous literature states that the unzipping process starts from the defect sites of CNTs.[30] Both the SEM and TEM images show that the ionic liquid treatment can effectively unzip CNT, thus makes the specific surface area of CNT sponge larger.

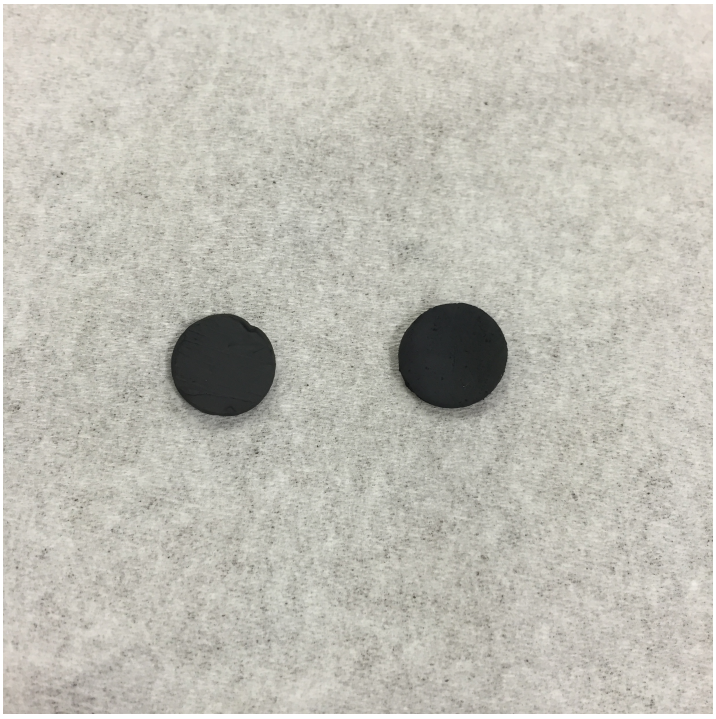

Fig. 3 The CNT sponge before (right) and after (left) 2hr ionic liquid treatment at 200°C.

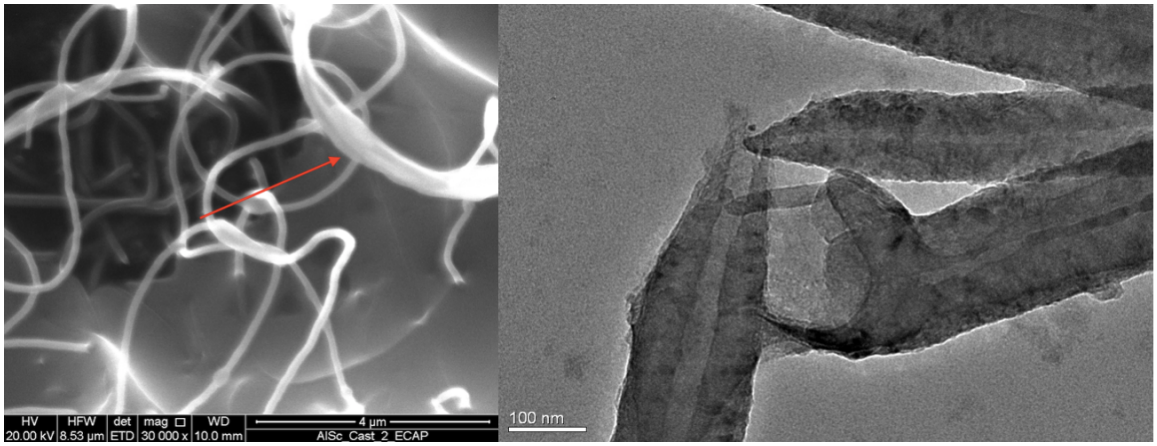

Fig. 4 SEM (left) and TEM (right) images of CNT sponge after 2hr ionic liquid treatment after 200°C. Red arrow indicates unzipped CNT.

And then we compared cell performances of the electrode using unzipped sponges as the sandwich electrode material with different treatment time, the temperature we set was at 200°C to ensure the ionic liquid will not boil. The sulfur loading in cathode of those cells was set at 8mg/cm^2, which makes the sulfur weight percent close to 50% in cathode. All of the cells were cycled at 0.1C charge/discharge rate. The result is shown in Fig. 5. When comparing with the performance of pristine sandwich electrode (blue dots, ~600mAh/g), the performance of electrode after 1hr ionic liquid treatment showed a little bit higher specific capacity (orange dots, ~700mAh/g) after 50 cycles. When the treatiment time increased from 1hr to 2hr, the capacity of the sample (gray dots) shows an further increase to ~800mAh/g after 50 cycles. However, the capacity will not always increase when the treatment time becomes longer. When the treating time increased to 8hr, the capacity only remained about 300mAh/g, which is only half of the capacity of pristine sample. This situation might because of the conductivity drop by the fluorine doping on the CNT.[40] Since the fluorine atom bonds with carbon in sp3 bonding, that means the π electron in the sp2 structure of CNT will be localized as the bonding electron between carbon and fluorine, thus it cannot transport electricity anymore. Among those results, since the 2hr treating time gave us obvious increase of capacity, we chose it as the ideal condition for our further testings.

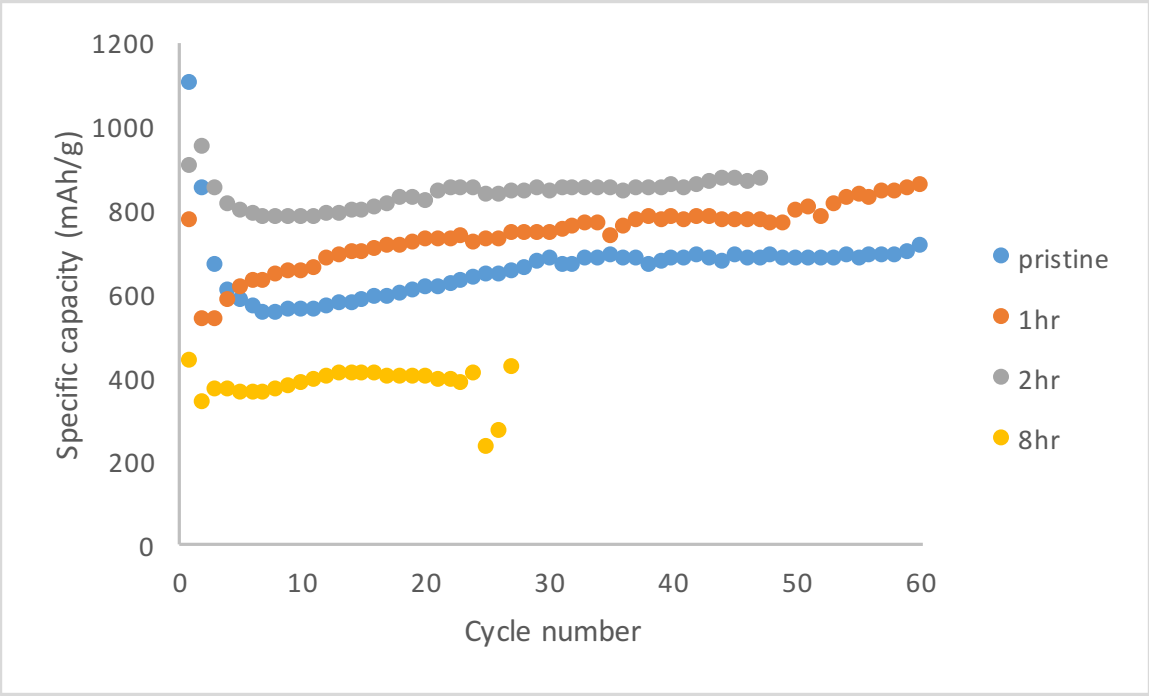

Fig. 5 Relationship between specific capacity and different ionic liquid treatment time with 8mg/cm^2 GO loading.

Although the specific capacity was increased from ~600mAh/g to ~800mAh/g after the ionic liquid treatment as we mentioned before, it was still far from its theoretical capacity 1675mAh/g. Which means about half of the sulfur was not utilized. We concluded that was because of the ultrahigh sulfur areal loading (8mg/cm^2) in our sample limited the sulfur utilization since the thick sulfur layer in our sandwich electrode will cause some of the sulfur at the middle could not contact with the conductive matrix (CNT sponge), thus could not be counted as active material. Another evidence is the capacity increase when the cycle number goes up. That represents the stabilization of electrode. When comparing with other literatures, their sulfur areal loading range often locates at 3~5mg/cm^2.[41, 42] In order to enlarge the the influence of ionic liquid treatment, we

reduced the sulfur areal loading to 3mg/cm^2, and then compared the difference between the pristine electrode and the sample after 2hr ionic liquid treatment. The cycle rate was set to 0.25C. As shown in Fig. 6, it is obvious that the ionic liquid treatment did enhance the cell capacity a lot. The pristine electrode possessed ~600mAh/g specific capacity, but the electrode after ionic liquid treatment obtained ~1150mAh/g specific capacity, which is almost 2 times higher than the original sample. The enhancement is because of the increased specific surface area of the CNT sponge. Since much surface area of the CNT sponge can be utilized to contact with sulfur and transport electrons, thus the capacity of the cell was increased. Furthermore, unzipped CNT sponge possesses the ability of adsorb the polysulfide molecules. For comparison, we immersed the pristine and unzipped CNT sponge into 0.2M catholyte, which is electrolyte containing Li_2S_6. At the beginning the catholyte colors of the two samples were the same. After 1 day, the color of the catholyte with unzipped CNT sponge inside became lighter, where the one with pristine CNT sponge still remains the same color. It can be explained by two different explanations. First, the unzipped CNT sponge has higher surface area, thus his higher ability for physisorption, thus can accommodate much polysulfide molecules. Second, the lone pair electrons on the doped fluorine group of the unzipped CNT sponge can catch the lithium polysulfide by electrostatic interaction.

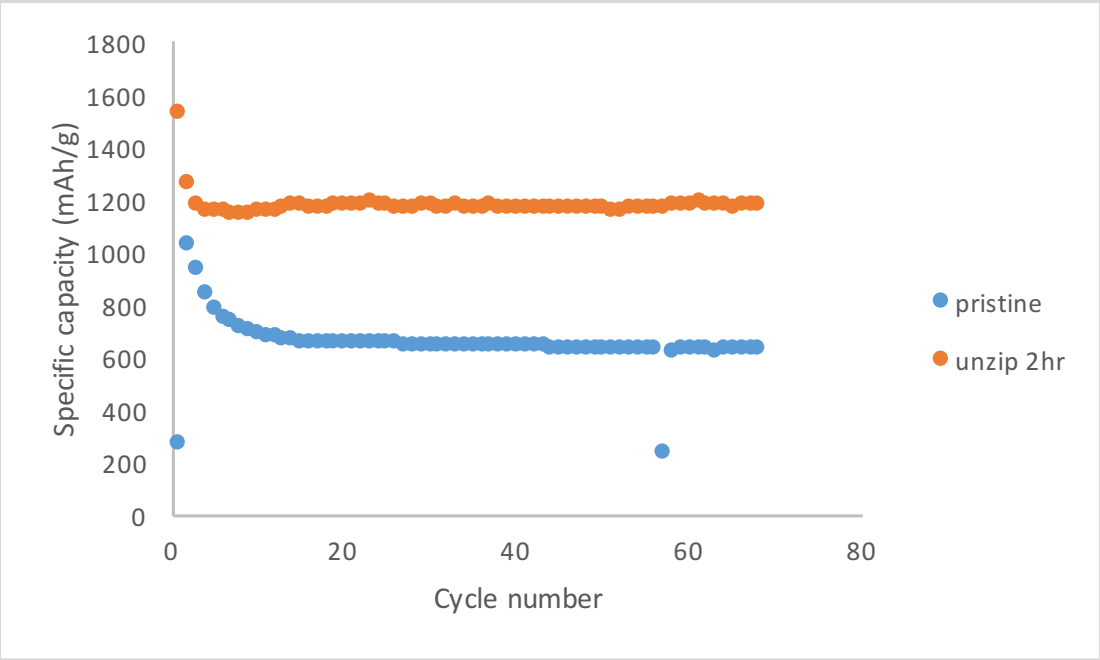

Fig. 6 Relationship between specific capacity and different ionic liquid treatment time with 3mg/cm^2 GO loading.

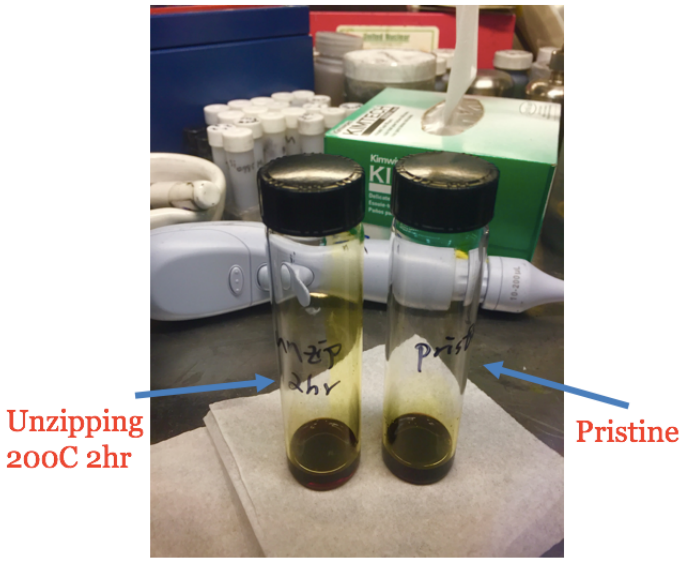

Fig. 7 Comparison of 3.6mg pristine and unzipped CNT sponge immersed in 0.8M catholyte for 1 day.

3.2 Influence of GO Layer

In our experiment, we deposited GO layer on top of the electrode, follow by the ozone plasma treatment to create some path for ions to diffuse. To check what kind of influence will be done by ozone plasma, we inspected the surface morphology of the CNT sponge after deposited GO with 1.3mg/cm^2 GO areal loading on top and ozone plasma treatment by SEM, which is shown in Fig. 8(a) to (f), where (a) and (b), (c) and (d), and (e) and (f) represent the top side view of GO deposited sponge after 10min, 40min and 80min ozone plasma treatment, respectively. After 10min ozone plasma treatment, GO layer still covered the whole surface of the electrode. Only some defects showed up, but no exposed CNT can be found. When the ozone plasma treatment time increased to 40min, more defects was created. It is much apparent that after 80min ozone plasma, even CNTs were exposed. Those sites can act as paths for ions to transport, instead of fully blocking the ionic transportation thus enhance the cell's rate capability.

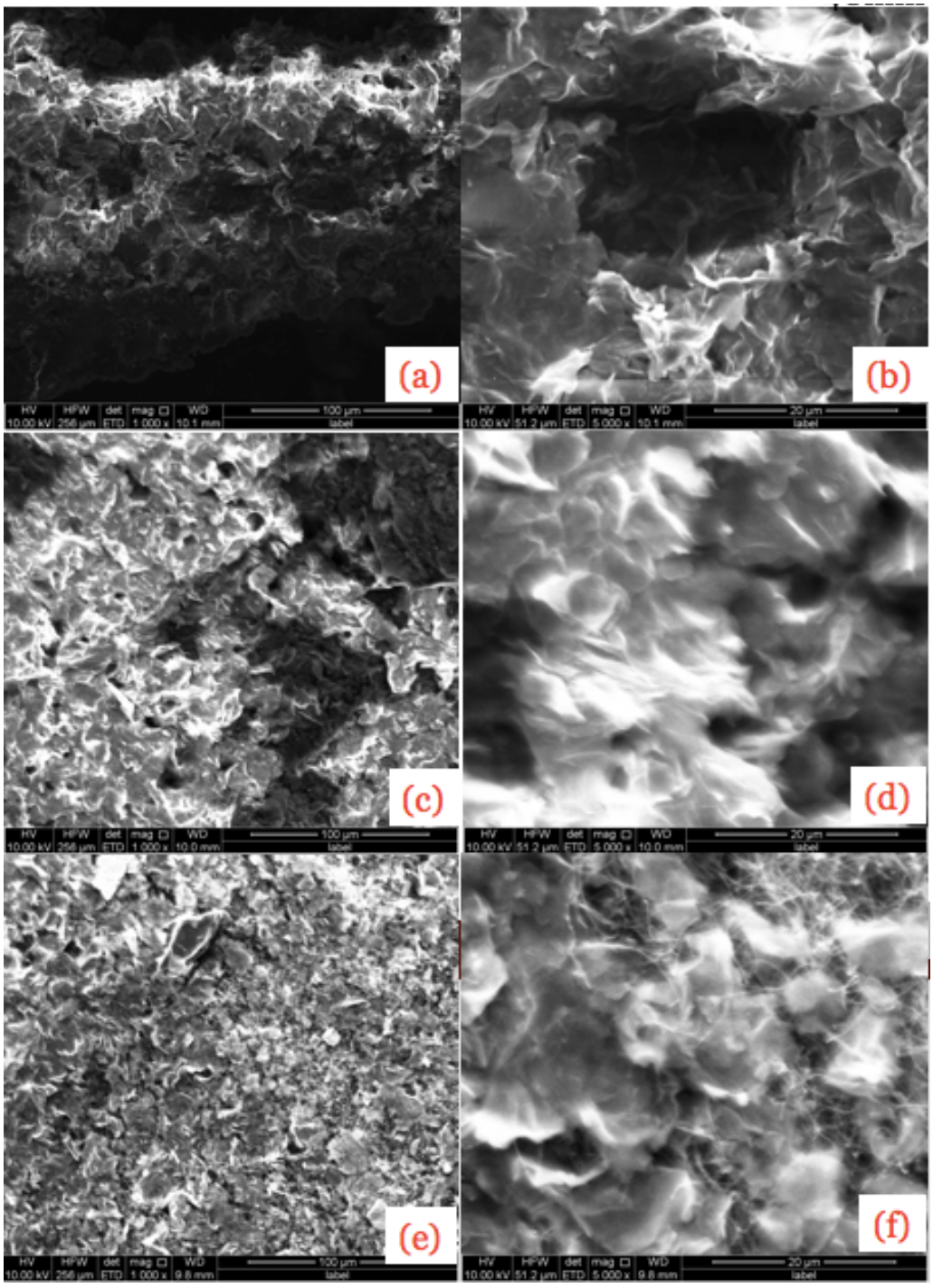

Fig. 8 The SEM images of GO deposited on sponge (GO loading: 1.3mg/cm^2) after 10min (a and b), 40min (c and d) and 80min (e and f) ozone plasma treatment.

Before investigating the influence of GO, it is necessary to check whether ozone plasma will affect the cell performance or not, since ozone plasma has the ability to functionalize CNT surface by doping functional groups contain oxygen, such as -OH and -COOH, the cell performance might be changed.[43] Hence, we compared the cell performance of the cells made with pristine CNT sponge sandwich electrode and CNT sponge after 160min ozone plasma treatment. The sulfur loading was set to 3mg/cm^2 to enlarge the influence, the cycle rate for charge and discharge was 0.25C, the result is shown below. It shows that the two cells perform almost the same performance, which can be explained by the ozone plasma will only affect small portion of CNT. To support this hypothesis, Sham et al.[43] reported treating CNTs having 10~20nm diameter by ozone plasma. After 1hr treatment, the oxygen content increased from 0.71% to 4.74%. When it comes to our large diameter CNTs, the influence of oxygen groups created by ozone plasma should be negligible if we assume the depth of graphitic layer of CNT be affected is the same, thus the cells show similar performance.

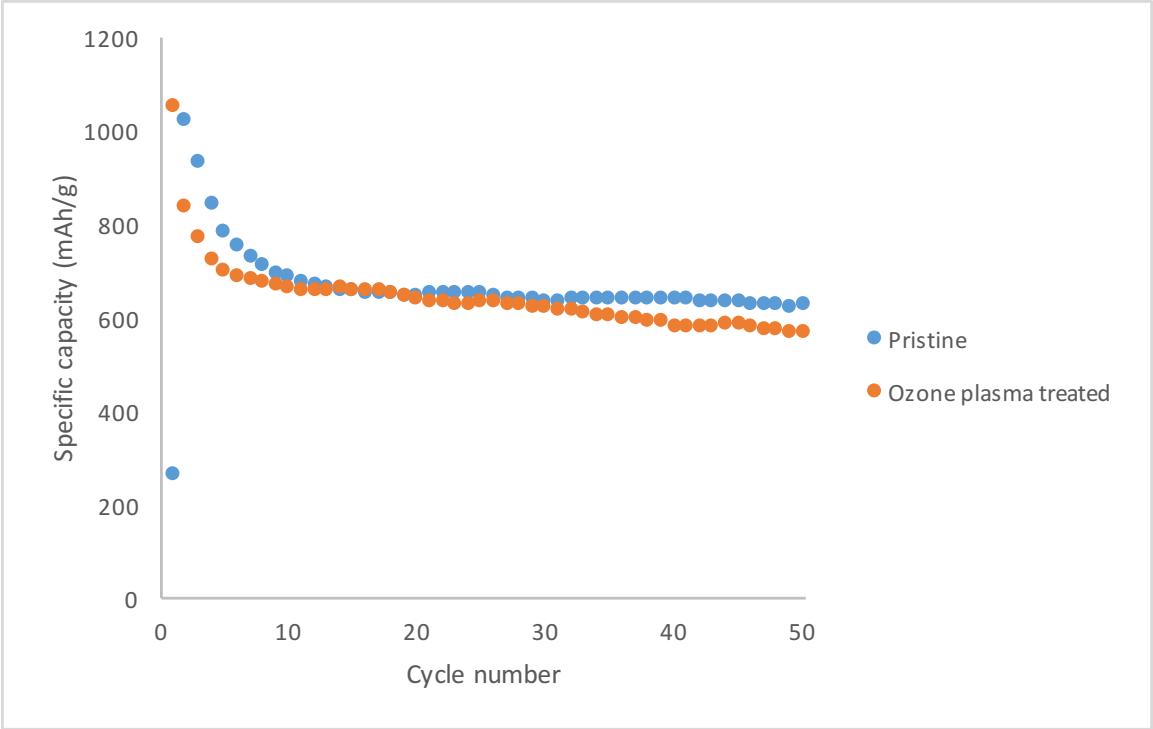

Fig. 9 Relationship between specific capacity of electrode before and after 160min ozone plasma treatment.

After checked the effect of ozone plasma to CNT sponge is small to the cell performance, we compared the influence of ozone plasma treating time when deposited GO on top of the electrode. The GO and sulfur areal loading in the following tests were set at 1.3 and 8 mg/cm^2, respectively. The sample without ozone plasma treatment and with 10min ozone plasma treatment could not be cycled (not shown in the below figure). When discharge, the cell voltage suddenly decreased to <1.7V. When charge, the voltage instantly exceeded the upper voltage limit (3.0V). This phenomena is because that the electrode surface is totally covered by GO layer. Without ozone plasma creating defect sites, there was no enough path for ion to transport. The sample after 40min ozone plasma treatment still showed lower capacity than the pristine electrode, probably

because although some path for ions diffusion was created by ozone plasma, the amount of path was still not enough for ion to diffuse through at 0.1C rate. When the ozone plasma treatment time increased to 80min, the performance of the cell became similar to the pristine electrode. And then we further increased the treatment time to 160 min, it showed higher performance then the previous sample, which might be contribute by the enough ionic transportation path created by ozone plasma, and the presence of GO hindered the polysulfide from shuttling. Hence, we choose 160min ozone plasma treatment time for further testing.

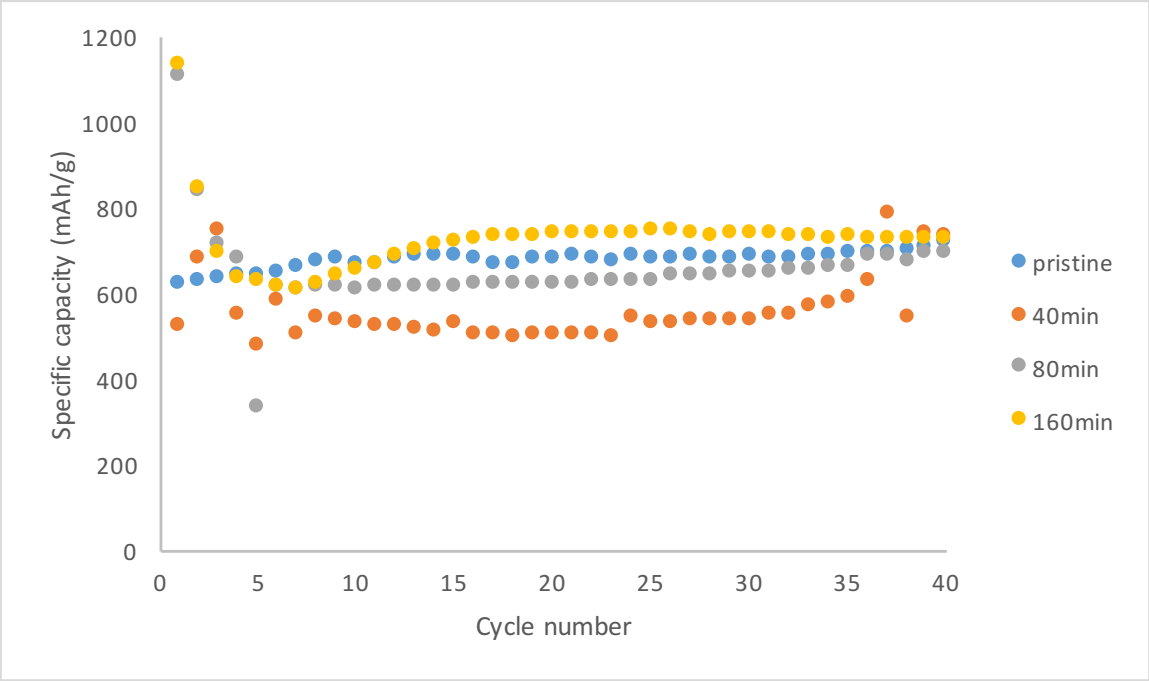

Fig. 10 Relationship between specific capacity and different ozone plasma treatment time with 1.4mg/cm^2 GO loading.

Another important factor has to be understand is the proper GO loading amount. In the following test, we chose 160min ozone plasma treating time and 8mg/cm^2 sulfur loading as our testing condition based on the previous result. The GO loading was varied from 0.7mg/cm^2 to 2.8mg/cm^2. The result is shown below.

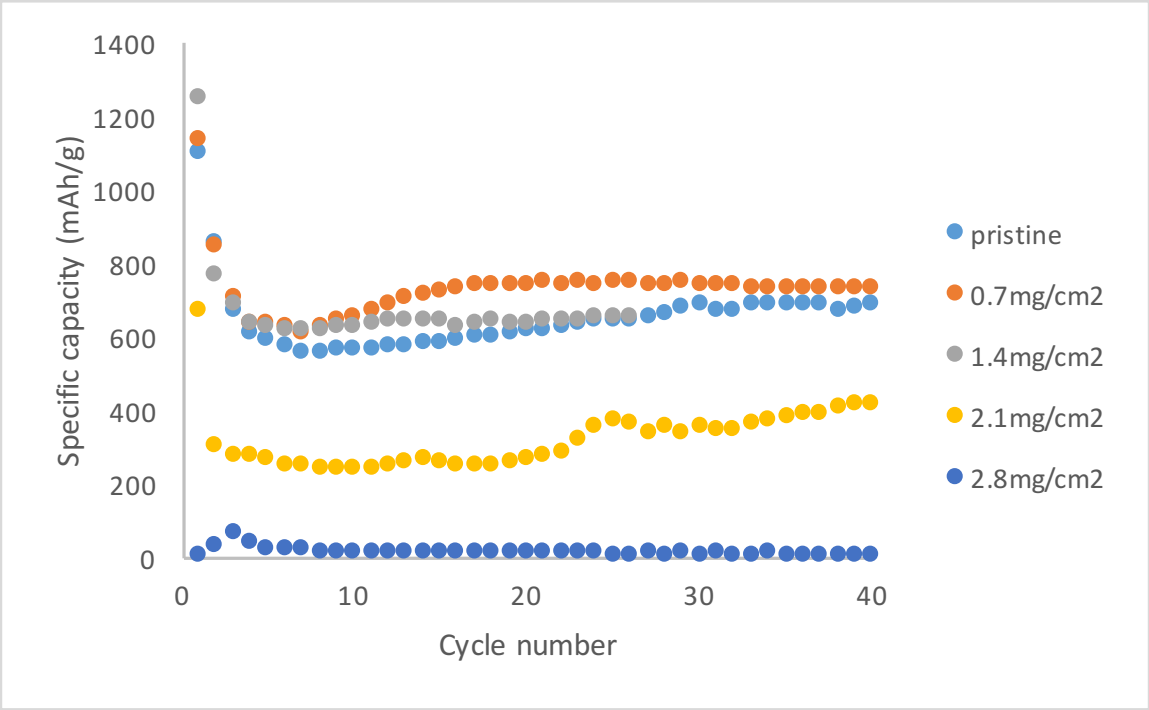

Fig. 11 Relationship between specific capacity and different GO loading.

It shows the capacity will increase at the beginning when increasing the GO loading, but followed by the decrease. The one with 0.7mg/cm^2 GO areal loading showed slightly higher capacity when comparing with the pristine sample. When the GO loading increases to 1.4mg/cm^2, the cell capacity drops a little bit when comparing with the 0.7mg/cm^2 GO loading sample. It is much apparent when increasing the GO loading to 2.1mg/cm^2 and 2.8mg/cm^2. The 2.1mg/cm^2 GO loading sample only possess about half

of the capacity when comparing the pristine sample, the 2.8mg/cm^2 sample almost had 0 capacity. That is because the excess GO might need longer ozone plasma treating time to get enough path for ion transportation. At the same time, the thickness of the electrode was increased by the GO additive, which made the ionic diffusion length longer, and then limited the cell capacity. The SEM image of the sample with 2.8mg/cm^2 GO loading is shown below. It is obvious that even after 160min ozone plasma treatment, the whole surface of electrode still fully covered by GO.

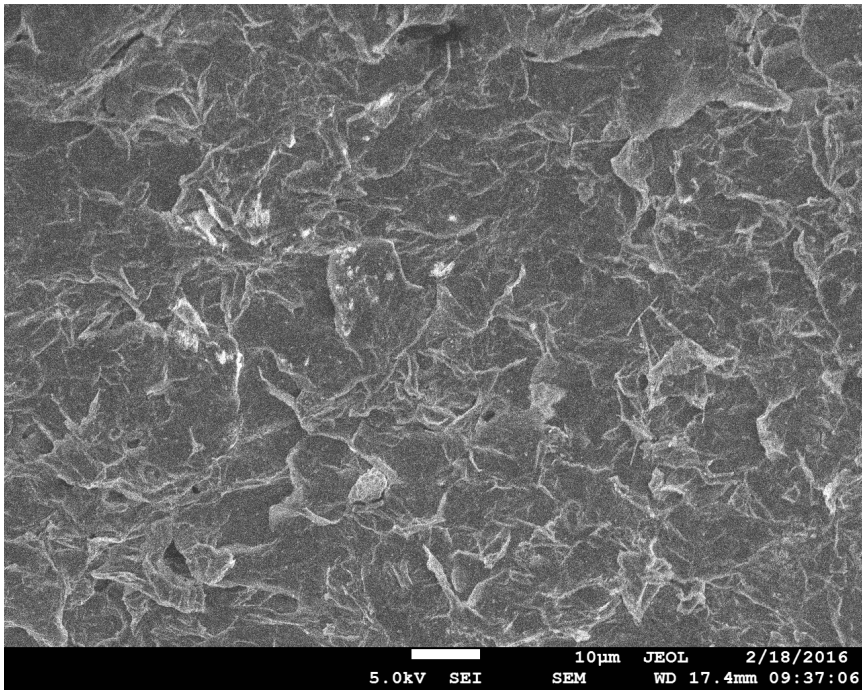

Fig. 12 The SEM image of CNT sponge covered with GO (areal loading 2.8mg/cm^2).

Similar as the previous tests, we compared the cells with lower sulfur loading (3mg/cm^2) to enlarge the GO influence. The 0.7mg/cm^2 GO loading and 160min ozone plasma treatment time conditions were chosen based on the previous results for further testing, the result shows in Fig. 13. It is apparent that the capacity of the sample after GO

deposition and ozone plasma treatment is about 900mAh/g, which is 1.5 times higher than the pristine sample. Which supports our hypothesis that GO can mitigate the polysulfide shuttling problem in Li-S battery, thus reduces the capacity fading of the cell and then increases the capacity by catching more active material on the cathode instead of diffuse out.

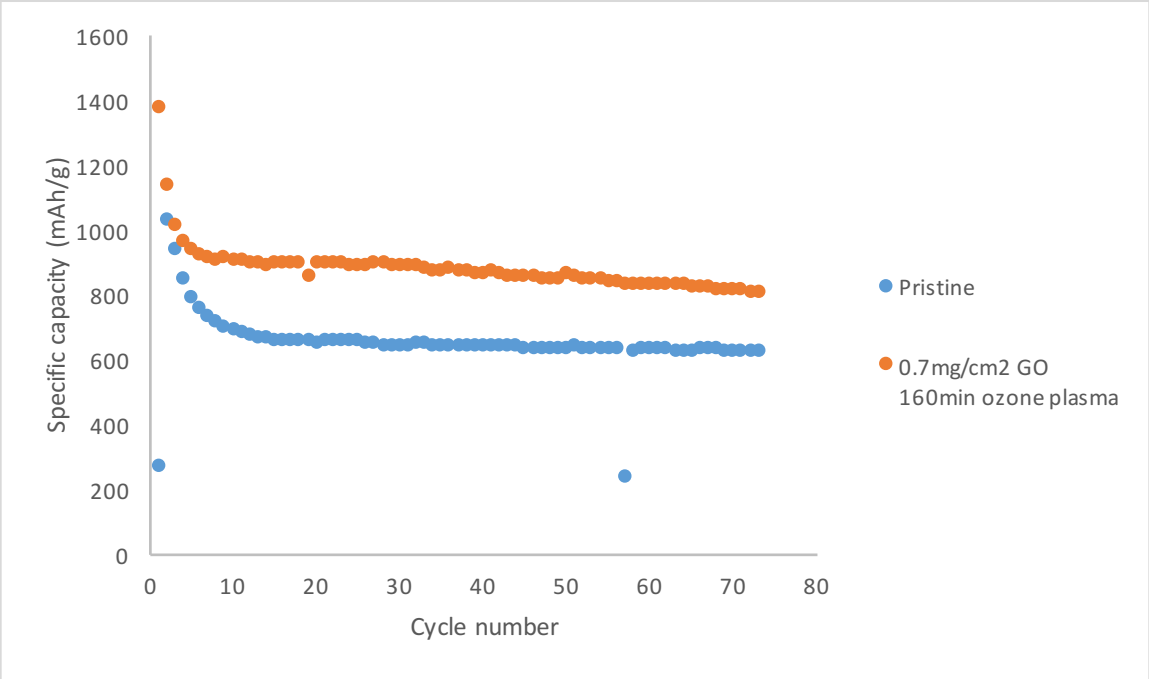

Fig. 13 Relationship between specific capacity of pristine electrode and electrode after 0.7mg/cm^2 GO deposition.

4. CONCLUSION AND FUTURE WORKS

In conclusion, we developed two different approaches, the unzipping CNT and depositing GO layer to enhance the cell performance of Li-S battery with sandwich electrode. For the Unzipping CNT, the capacity of the sample after 2hr ionic liquid treatment at 200°C possesses specific capacity as high as ~1200mAh/g, where the pristine electrode only has ~600mAh/g after 60 cycles at 0.25C cycle rate. When it comes to depositing GO layer, the capacity remains ~900mAh/g after 70 cycles at 0.25C, which is higher than the pristine electrode (~600mAh/g). Both of the results show the improvement of cell performance.

In future, further material characteristic jobs should be done, which shows below:

- Brunauer–Emmett–Teller (BET) analysis

  The BET analysis can determine the specific surface area of our samples. The test is to quantitively support our hypothesis that the unzipping procedure can increase the specific surface area of CNT sponge.

- Raman confocal microscope
- Fourier transform infrared spectroscopy (FTIR)
- X-ray photoelectron spectroscopy (XPS)

  Those three testing above can analyze the chemical bonding in the sample. These testing are to check whether there is any bonding between sulfur/oxygen in GO, and sulfur/fluorine in unzipped CNT as the literature states. Thus gives support to our results.

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